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PATENT SPECIFICATION

DRAWINGS ATTACHED

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Int. Cl.:—C 23 c 3/02

COMPLETE SPECIFICATION

Aqueous Electroless Plating Solution

We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing under the laws of the State of New York in the United States of America, of

5 Armonk, New York 10504, United States of America (assignees of ARNOLD FRIEDRICH SCHMECKENBECHER) do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it

10 is to be performed, to be particularly described in and by the following statement:—

This invention relates to an aqueous solution for electrolessly depositing a magnetic material containing nickel and iron, and is applicable to the production of magnetic films for use as storage and switching elements in data processing and computer machines.

Even since M. J. Blois, Jr., described in The Journal of Applied Physics, Volume 26, 20 p. 975, 1955, the preparation of thin films of 80:20 (by weight), nickel-iron, in the presence of an orienting magnetic field to induce uniaxial anisotropy, considerable effort has been expended to develop a practical thin film storage device for computers. These films exhibit two stable states, along the preferred direction of magnetization, corresponding to positive and negative remanence. With the application of selected electrical signals along conductors, in contact with, or in the vicinity of, the film, the magnetization is switched from one of its remanent states to the other to represent intelligence. The state of magnetization, corresponding to this intelligence, 30 is recognizable on the application of further selected electrical pulses.

Although, in general, it is recognized that the permalloy family, that is, compositions containing from 15 to 45 per cent iron and 40 55 to 85 per cent nickel, offer the most promising films for these applications and that conventional techniques such as vacuum deposition, electroplating, cathode sputtering, and pyrolytic methods are available, much remains 45 to be accomplished, before a film from one of

those techniques is adaptable for use in a data processing or computer machine. Problems are encountered in reproducibility and in the uniformity of characteristics obtained with the magnetic films from these techniques.

One method which has not received the attention that the other methods have, is that of chemical reduction or electroless plating. Nickel, nickel-cobalt and other metal alloy films have been deposited on an active or catalytic surfaces by the reduction of the metal salts with hypophosphite but few advances have been made in the production of nickel-iron films where the major constituent of the film is nickel. In those instances where nickel-iron films have been deposited electrolessly, the resulting films were disturb sensitive and exhibited a low one to zero difference signal. The former property, disturb sensitivity, is a measure of the ability of a film to remain in a selected magnetic remanent state in the presence of stray magnetic fields; the more disturb sensitive a film is, the more precisely must the switching fields conform to specified magnitudes and directions. The latter quantity, the one to zero difference signal, is a measure of the signal available for sensing intelligence on interrogation, the lower the signal is, the more difficult it becomes to accurately discriminate between noise signals and intelligence signals, and, the greater are the demands placed on the sensing circuits involved. Accordingly, the magnetic films produced from such processes lack economy and reliability.

Now what has been discovered is that these aforementioned disadvantages with the chemical reduction of a nickel-iron film may be avoided or reduced by using an electroless plating solution in which interalia a hypophosphite ion concentration is maintained between 2 and 7.00 grams/litre. While the reasons for this are not well understood, a working hypothesis has been formulated. In the electroless solution containing between 2 85 90

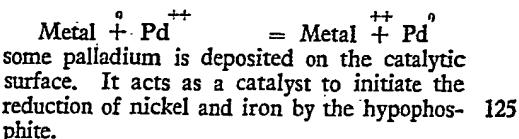
- and 7.00 grams/litre of the hypophosphite ions, the plating rate is slower than with a higher concentration of hypophosphite. This allows for more interaction and growth of secondary ingredients which may favour high resistivity, and, in turn, less eddy current formation, and, thereby provide more complete switching of the film.
- Another factor, along with the hypophosphite ion concentration, which directly affects the plating operation, is the pH value. It is found desirable that the solution should have a high pH value, that is, a pH of at least 8. With solutions having a pH lower than this, very little iron is deposited in the film, however large the amount of ferrous ions in the solution. Optimum results are obtained when the pH is maintained at a value of 10 or higher.
- According to one aspect of the present invention, there is provided an aqueous solution for electrolessly depositing a magnetic material containing nickel and iron, said solution comprising water soluble nickel and iron salts in concentrations sufficient to provide a nickel to ferrous ion ratio between 1 and 5, hypophosphite ions in concentrations between 2 and 7 grams/litre, the substance which provides said hypophosphate ions being the only reducing agent for said salts in said solution, and sufficient hydroxyl ions to maintain the pH at at least 8, and one or more complexing or sequestering agents for forming stable water soluble complexes with the nickel and iron ions of said salts.
- The electroless deposition process is based on the controlled autocatalytic reduction of the nickel and iron by means of the hypophosphite anions. Nickel-iron phosphorous alloys are chemically deposited from such an electroless solution, by placing in contact therewith substrates which are composed of copper, nickel, cobalt, iron, steel, aluminium, zinc, palladium, platinum, brass, manganese, chromium, molybdenum, tungsten, titanium, tin, silver, carbon, or graphite, or alloys containing any of these. The catalytic nature of these materials causes the reduction of the nickel and iron to the nickel-iron-phosphorous alloys by the hypophosphite anions present. Of course it will be realised by those versed in the art that non-catalytic surfaces such as non-metallic materials may receive beneficial treatment, by such a process, where the surface of the non-catalytic material is first sensitised, by producing a film of one of the catalytic materials on its surface. This is accomplished by a variety of techniques known to those skilled in the art.
- When electrolessly depositing nickel and iron from an alkaline electroless plating solution, the presence of a compound forming water soluble nickel complexes is necessary in order to prevent precipitation of the nickel as a hydroxide or hypophosphite. The

precipitation may be avoided with the addition of sufficient ammonia or ammonia salts to form the nickel hexamine complex ion. To prevent the precipitation of the iron as ferrous ions, tartrate ions can be added to keep the concentration of the ferrous ions below their solubility limit. Similarly, the activity of the hypophosphite ion can be regulated by adjusting the free alkali content as measured by the hydroxyl ion content of the solution, this being done with the addition of agents which in aqueous solution have a basic reaction or water soluble bases such as sodium hydroxide, potassium hydroxide, ammonium hydroxide, or lithium hydroxide.

It will be recognised by those versed in the art that other complexing or sequestering agents besides the ammonia and tartrate ions are usable in a solution according to the invention. These include organic complex forming agents containing one or more of the following functional groups: primary amino group ($-NH_2$), secondary amino group ($>NH$), tertiary amino group ($>N-$), imino group ($=NH$), carboxy group ($-COOH$), and hydroxy group ($-OH$). These organic agents may be used in concentrations of 5 to 100 grams/litre, preferably about 25 grams/litre. The preferred agents are rochelle salt, seignette salt, tartaric acid, ammonia, ammonium hydroxide, and ammonium chloride. Related polyamines and N-carboxymethyl derivatives thereof may also be used. Cyanides may not be employed since the plating process will not function in their presence.

The nickel and ferrous ions may be employed in the form of any water soluble salt which is not antagonistic to the plating process. They may be furnished in the form of chlorides, sulfates, acetates, sulfonates, and mixtures thereof.

In carrying out the electroless plating process the article to be plated, that is, the catalytic material, is properly prepared by mechanical cleaning and degreasing according to the standard practice of the industry. If the material to be plated consists of copper or a copper alloy, the article is then further cleaned by dipping in 10% hydrochloric acid for about 30 seconds in room temperature, then activated by dipping in a 0.1% palladium chloride solution for about 15 seconds and at room temperature. Due to an exchange reaction



The activated catalytic material is then brought into contact with the plating solution which has been heated to the desired temperature whilst it is covered with a layer

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- of Xylene. The plating solution is covered with the Xylene to prevent, as much as possible, the oxidation of the ferrous ion to the ferric ion, an undesirable ingredient in the solution, if it is present in concentrations of more than about 200 mg./l. of Fe^{+++} . The catalytic surface is maintained in contact with the plating solution until a nickel-iron-phosphorous alloy is formed on the surface of the desired composition. Where anisotropic properties are desired, the plating is performed in the presence of a magnetic field, while if isotropic characteristics are preferred, the plating is performed without the application of any external magnetic fields.
- In this manner, nickel-iron-phosphorous alloy films may be formed having suitable characteristics for computer applications. The preferred alloys contain substantially from 15% to 35% by weight iron, 65% to 85% by weight nickel, and 0.25% to 2% by weight phosphorous, greater signal differences being obtained with ferromagnetic films containing substantially 24 to 35 percent by weight iron, 65 to 76 percent by weight nickel, and 0.25 to 2 percent by weight phosphorous. The optimum characteristics for data processing applications are obtained with an alloy containing substantially from 28% to 30% by weight iron, 70% to 72% by weight nickel, and 0.5% by weight phosphorous. The alloys may have a magnetic remanence between 0.05 and 0.35 maxwells, and a coercivity between 2 and 6 oersteds. These alloy films appear silver metallic with small dark dots visible under the microscope. At higher thicknesses they turn from golden brown to dark brown. They have a face centred cubic structure and their surface is corrugated, and, electronic microscopes at 48,000 X show an agglomeration of balls with their diameter in the order of 1000\AA . These films in thicknesses of about $20,000\text{\AA}$ when exposed to driving fields switch their magnetisation within relatively short times. Their switching speeds are in the order of 2 to 6 nanoseconds with an applied field of 20 oersteds. Their voltage signal is a sharp symmetrical peak, typical of rotational switching. Furthermore, they produce large one to zero signals and exhibit a low disturb sensitivity.
- The invention will be further explained by way of example with reference to the accompanying drawings in which:—
- Figure 1 is an isometric diagram of a substrate which may be coated with a magnetic film using an aqueous solution according to the invention;
- Figure 2 is a cross-sectional view of an electroless plating apparatus; and
- Figures 3 to 9 are various graphs used to explain and illustrate the invention.
- Figure 1 shows a conductive strip which has a chain-like configuration and on which a magnetic film is to be deposited. Figure 1 shows several elements 10 of the chain-like configuration prior to undergoing the magnetic deposition. The conductive strip element 10 includes toroidal or elliptically shaped portions 14 which are electrically coupled by neck portions 11. The toroidal or elliptically shaped portions 14 form the storage unit. The conductive strip storage device is described and claimed in the complete specification of our copending application No. 12005/65 (Serial No. 1052647).
- In forming the conductive strip, two ounce (.0028 inches in thickness) rolled copper foil is preferred, although, as heretobefore mentioned, any catalytic surface is usable. The copper foil is cleaned in a 10% solution of hydrochloric acid, rinsed with water, and dried. Conventional photoresist is applied, and the material is then exposed through a positive mark, to a zenon arc lamp or equivalent light source for a few seconds. The material is then etched in 30° Be ferric chloride, immersed in photographic fixer and the required chain-like structure developed according to standard techniques.
- Following this, the chain-like structure is again rinsed in hydrochloric acid, washed in water, then it is dipped for about 15 seconds at room temperature into a solution of 1 gram of purified palladium chloride in a mixture of 1000 milli-liters of water and 1 milli-liter of concentrated hydrochloric acid for sensitising. Following this, the chain-like structure is again rinsed with water.
- The substrate is then ready for receiving the magnetic film. To do this, as illustrated in Figure 2, a series of conductive strips 15 are mounted along a rack 17 and inserted into container 19 which holds the required electroless solution 21, covered with a layer of Xylene 23, which is used to prevent oxidation of the cations of the electroless solution. The rack is mounted within the container on supports 25, positioned along the sides of the container. The container is inserted into a vat 27 which contains a liquid medium 29, such as water or oil, for maintaining a constant bath temperature. The container is surrounded by Helmholtz coil 31 where anisotropic characteristics are desired in the film, while, if isotropic characteristics are sought, the coil 31 is not used.
- The electroless solution utilised contains the constituent materials in the concentrations as shown in the following chart which includes as complexing agents ammonium salt and a tartaric salt. It is to be noted that other complexing agents are usable as heretobefore discussed and is further brought out in the discussion that follows. The chart gives the concentration in grams/litre of aqueous solution of each ion constituent present in the solution. In each instance, the minimum, optimum and maximum concentration for each

compound, salt and ion constituents are given in tabular form.

CHART 1

		Grams/Liter		
		Min.	Preferred	Max.
Electroless Solution				
nickel ions	Ni ⁺⁺	0.3	3.30	30
ferrous ions	Fe ⁺⁺	0.1	1.1	10
hypophosphite ions	(H ₂ PO ₂)—	2.00	3.5	7.0
tartrate ions	(C ₄ H ₄ O ₆) =	5	17.5	80
nickel to ferrous ion ratio	Ni ⁺⁺ /Fe ⁺⁺	1.00	3.0	5
pH		8	11.5	13
ammonium ions		0.6	64	300
Temperature		50° C.	75° C.	95° C.
time		5 minutes	45 minutes	120 minutes
plating rate		150 A°/min.	500 A°/min.	1500 A°/min.

It should be noted that for example the minimum concentrations of nickel and ferrous ions given in the column headed "Min." are not inconsistent with the nickel to ferrous ion ratio given in the same column. Thus if it was desired to use a solution containing the minimum ferrous ion concentration of 0.1 grams/liter, it would not of course be possible for that solution to have the minimum nickel to ferrous ion ratio of 1.0, but the solution could have a nickel to ferrous ion ratio of say 3.0.

As it is noted from the above chart, the preferred ratio of the nickel ions to ferrous ions in this plating solution should be approximately 3 to 1, the hypophosphite ions about 3.5 grams/liter, and the pH maintained at about 11.5 develop the optimum characteristics available from the electroless solution.

The following are illustrative examples of the magnetic film composition, the electroless solution, the process of depositing the same, the working conditions for the procedure.

EXAMPLE 1

Following the preparation of the copper substrate as described heretofore, the substrate is immersed in an electroless solution. The electroless solution was formed by mixing 25 milliliters of a solution containing 240 grams/liter of nickelous chloride (NiCl₂ · 6H₂O) and mixed with about 150

milliliters of water. 12.5 milliliters of a solution containing 200 grams/liter of sodium hypophosphite (NaH₂ PO₂ · H₂O) and 25 milliliters of a solution containing 600 grams/liter of sodium potassium tartrate (KNa C₄ H₄ O₆ · 4H₂O) are then added. The mixture is made up to 250 milliliters by the addition of water. 100 milliliters of a solution containing 3.5 grams ferrous ammonium sulfate (NH₄)₂SO₄ · FeSO₄ · 6H₂O and 100 milliliters of ammonium hydroxide solution containing 28 to 30 percent NH₃ are added.

This bath contains:

3.30 grams/liter Ni⁺⁺
1.10 grams/liter Fe⁺⁺
3.44 grams/liter (H₂PO₂)
17.5 grams/liter (C₄H₄O₆)

and
223 milliliters/liter ammonium hydroxide solution (28% NH₃).

The pH value was maintained at about 11.5 and the ratio of nickel ions to ferrous ions at about 3 to 1. The solution was poured into the container, covered with about $\frac{1}{2}$ inch thick layer of the Xylene and heated by suitable means to maintain the bath about the container at about 75°C. The activated substrates hanging from the rack are positioned in the solution for about 40 minutes. Both anisotropic and isotropic films were made in

- separate runs. In the case where the anisotropic films were made, a homogeneous linear magnetic field of 40 oersteds was applied along the longitudinal axis of the substrates.
- 15 Following the deposition, the substrates were removed, rinsed with water and dried.
- Curves as depicted in Figure 3 were plotted for the magnetic films coated on the substrates. These curves indicate the type of 10 magnetic characteristics which are available with the film when utilised as a memory storage element.
- These curves are obtained with a constant word pulse while varying the bit pulse. The 15 memory element of Figure 1 is switched, that is, the magnetic remanence switched from one stable state to the other by the application of longitudinal and transverse pulses. The longitudinal pulse, the word pulse, is applied 20 along the longitudinal axis of the element, that is, along the direction indicated by Arrow A, while the transverse pulse, the bit pulse, is applied along conductor 22 (shown for one element) through the aperture of the 25 element. To write in the element, a unipolar word pulse of about 640 milliamperes in amplitude and 20 nanoseconds rise time is passed along the longitudinal axis of the element. A bit current with a time lag of 30 about 55 nanoseconds is passed through conductor 22 going through the aperture of the element. The bit current has an amplitude increasing from zero to 600 milliamperes and a rise time of 30 nanoseconds. Reading is 35 accomplished on the leading edge of the word pulse while writing is performed when the word pulse and bit pulse overlap. By maintaining the word pulse constant and varying the bit pulse over the ranges indicated in 40 FIGURE 3, the waveform for the undisturbed one signal (uV_1) is obtained. To obtain the waveform for the disturbed one signal dV_1 , the same procedure as for the undisturbed one signal uV_1 is followed, but, after the bitpulse 45 is applied, the stored information is disturbed by applying from 500 to 1000 bit pulses of the appropriate polarity and of amplitude to 20% higher than the previous bit pulse with a rise time of 30 nanoseconds. The undisturbed zero uV_z is obtained, as the undisturbed one uV_1 , but the polarity of the bit pulse is reversed to that of the polarity for the undisturbed one uV_1 . Similarly, the disturb zero dV_z is obtained in a similar fashion to 50 the disturbed one dV_1 , with the polarities of the bit pulse being reversed as described for the undisturbed one uV_1 .
- These curves give an indication of the 55 available one to zero difference signal for sensing intelligence in the operation of the memory element. What is desired, in such a curve, is that the disturbed one dV_1 and zero signals dV_z be large over a wide range of bit currents and, in particular, it is desired that the signals be large at low bit currents, that is, the curves rise fast from the origin. It is also desired that the curve of the disturbed one dV_1 be fairly close to the curve of the undisturbed one uV_1 signal and, similarly, that the disturbed zero dV_z curve be fairly close to the undisturbed zero uV_z curve. That is, it is desired that the distance f between the undisturbed one uV_1 and disturbed one dV_1 and the distance g between the undisturbed zero uV_z and disturbed zero dV_z signal be at a minimum. Further, it is desired that the cross-over point for the disturbed one dV_1 and disturbed zero dV_z , that is, the point K where the disturb one dV_1 and disturb zero dV_z touch the abscissa of the graph, be maximized as far to the right from the origin as feasible. As these conditions are obtained with the curve, large zero and one signals are obtained, a wide range of bit currents including bit currents of low amplitude are available 70 for switching the intelligence in the memory element, lowering the uniformity requirements for the elements in a large memory. Also, the intelligence in the memory element is not readily eliminated by accidentally applied stray fields or through the influence of adjacent fields. On the other hand, if these conditions are not met by the curve, that is, if the disturbed zero dV_z and disturbed one dV_1 signals are small, if they are not of approximately the same signal magnitude, if the range of bit currents yielding large one and zero signals is narrow, or the cross-over point is not maximized to the right, the film yields 75 a low signal on sensing and it requires very uniform memory elements with exactly the same range of usable bit currents. Further, the element has little resistance to the influence of stray fields.
- For example, the difference signal between one and zero was between 30 and 50 millivolts over a range of bit currents of about 100 milliamperes, with the cross-over point at about 300 milliamperes. These parameters were determined from elements such as that shown in FIGURE 1 of about 0.02 inches outer diameter, 0.015 inches inner diameter, and with a thickness of about 0.0025 inches. The thickness of the resulting film was about 18,000 Å and the composition of the magnetic film contained 28% iron, 71.5% nickel, and 0.5% phosphorous.
- EXAMPLE 2.
- Essentially the same procedure as that described in Example 1 was followed but the plating time was about 10 minutes. The film had a difference signal of about 10 millivolts with a cross-over point at about 400 milliamperes. The film contained 32% iron, 67.5% nickel, and 0.5% phosphorous and was deposited to a thickness of about 8000 Å.
- EXAMPLE 3.
- The same procedure as Example 1 was followed but the plating time was about 60

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- minutes. The film had a difference signal of about 5 millivolts with a cross-over point of about 150 milliamperes. The film contained 5 32% iron, 67.5% nickel, and 0.5% phosphorous, and was deposited to a thickness between 25,000 to 35,000 Å.

EXAMPLE 4.

- 10 The same procedure as Example 1 was followed but the solution contained 3.5 grams/liter sodium hypophosphite, the plating time was maintained at about 75 minutes. The resulting film exhibited a one to zero difference signal ratio of about 12 millivolts, and had a 15 cross-over point at about 240 milliamperes. The film contained 26% to 28% iron, 72% to 74% nickel, and 0.5% phosphorous, and was deposited to a thickness between 9,000 to 15,000 Å.

EXAMPLE 5

- 20 The substrate was treated as described in Example 1, but the electroless solution contained 5.4 grams/liter of sodium hypophosphite. The plating time was about 35 minutes. 25 A one to zero difference signal ratio of about 16 millivolts was obtained with a cross-over point of about 350 milliamperes. The film contained about 31% iron, 69% nickel, 0.5% phosphorous, and was deposited to a thickness of about 15,000 Å.

EXAMPLE 6.

- 30 The same procedure as utilized in Example 1 was followed, but the electroless solution contained 11.8 grams/liter of sodium hypophosphite. The plating time was 25 minutes. 35 A one to zero difference signal noise ratio of about 2 millivolts was obtained with a cross-over point at 120 millampers. The resulting film contained 26% iron, 73% nickel, and 40 1.0% phosphorous, and was deposited to a thickness of about 20,000 Å.

EXAMPLE 7.

- The same procedure as Example 1 was followed, but the concentration of the nickel ions was maintained at 0.33 grams/liter and the concentration of the ferrous ions at 0.11 grams/liter. The plating time was maintained at 80 minutes.

EXAMPLE 8.

- 45 Essentially the same procedure was followed as for Example 1, but the nickel ion concentration was maintained at 22 grams/liter and the ferrous ions at 7.3 grams/liter. The plating time was maintained at 30 minutes.

EXAMPLE 9.

- 50 Essentially the same procedure as utilized in Example 1 was followed, but the concentration of ferrous ions was maintained at 2 grams/liter which corresponds to a nickel to ferrous ion ratio of about 1.66. The plating time was 60 40 minutes. The film on examination indicated a one to zero difference signal ratio of about 35 millivolts with a cross-over point of 200 milliamperes. The film contained 25% iron, 73% nickel, 2% phosphorous, and was deposited to a thickness of about 18,000 Å.

EXAMPLE 10.

- 65 Essentially the same procedure as utilized in Example 1 was followed, but the ferrous ion concentration was maintained at 0.8 grams/liter, which corresponds to a nickel to ferrous ion ratio of about 4.16. The plating time was 70 about 40 minutes. The one to zero difference signal of about 20 millivolts was obtained at a cross-over point of about 300 milliamperes. The film contained 29% iron, 71% nickel, 0.25% phosphorous, and was deposited to a thickness of about 12,000 Å.

75 As brought out by the chart below, the preferred ingredients for utilization in the process may vary over a wide range.

CHART 2

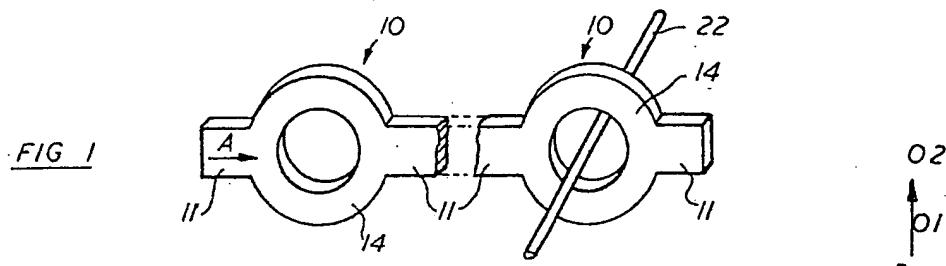
Plating Solution Compounds	Grams/Liter		
	Minimum	Optimum	Maximum
NiSO ₄ .6H ₂ O (nickel sulfate)	1.2	13.3	120
(NH ₄) ₂ SO ₄ .FeSO ₄ .6H ₂ O (ferrous ammonium sulfate)	0.7	7.5	70
NaH ₂ PO ₂ .H ₂ O (sodium hypophosphite)	3.2	5.8	10
KNa C ₄ H ₄ O ₆ .4H ₂ O (sodium potassium tartrate)	10	30	150
NH ₄ OH(28—30% NH ₃) (in milliliters/liter) (ammonium hydroxide)	40	100	150

- Now with reference to FIGURES 4 through 9, it will be noted that various process parameters have been plotted against the sodium hypophosphite concentration. These figures further indicate that hypophosphite concentration is important in obtaining the required magnetic characteristics for a magnetic film for computer applications. From these plots it is seen that in solutions where the sodium hypophosphite concentration exceeds 10 grams/liter, or in terms of the hypophosphite ion, exceeds 7.0 grams/liter, the magnetic characteristics required for the storage of intelligence fall off. Now with particular reference to FIGURES 4, 5, and 6, it will be noted that several parameters are plotted against sodium hypophosphite. In FIGURE 4, magnetic remanence B_r in maxwells is plotted against the reducing agent; in Figure 5, coercivity H_c in oersteds is plotted against it, and in Figure 6, the cross-over point is plotted against the sodium hypophosphite concentration. It will be noted that for each of these plots there is a rather small range of hypophosphite concentration which is available, if each of the parameters, for each of the plots, is to be at its most beneficial quantity for the magnetic film. Similarly, for Figures 7, 8 and 9, various parameters are again plotted against the sodium hypophosphite concentration where the abscissa is the same scale for all three plots. Here again note there is a small range of sodium hypophosphite concentration for which each of these parameters has a value beneficial for the magnetic film. Figure 9 indicates that plating rate decreases with decrease in hypophosphite content, and as previously stated, a slow plating rate is thought to be desirable for obtaining the required characteristics in the magnetic film. As brought out by the first chart given in the specification, it is not desirable to have a plating rate greater than 1500 A° per minute.
- As previously mentioned, the nickel and ferrous ions may be furnished to the solution in the form of any water soluble salt, such as chlorides, sulfates, acetates, sulfonates and mixtures thereof as long as the anions do not interfere with the plating. Similarly, the hypophosphite ions may be furnished in the form of water soluble salts or various bases such as sodium hypophosphite, potassium hypophosphite, hypophosphorous acid and mixtures thereof.
- Surface active substances may be added to a solution according to the invention such as sodium lauryl sulfate, as long as the substances do not interfere with the plating reaction. Exaltants also may be added, to increase the rate of deposition by activating the hypophosphite anions, such as succinic acid, adipic anions, alkali fluorides and other exaltants which are known to those in the art. Stabilizers may be added in minute concentrations such as 10 parts per billion. These may be stabilizers such as thiorea, sodium ethylxanthate, lead sulfate and the like. Also, pH regulators and buffers such as boric acid, disodium phosphate and others may be included in the solution.
- Other metal ions may be added to the electroless plating solution in their lowest oxidation states, such as cobalt (Co^{++}), molybdenum (Mo^{++}), chromium (Cr^{++}), and the like. These cations increase the coercive force of the films and thereby increase the stability against disturb fields.
- WHAT WE CLAIM IS:—
1. An aqueous solution for electrolessly depositing magnetic material containing nickel and iron, said solution comprising water soluble nickel and iron salts in concentrations sufficient to provide a nickel to ferrous ion ratio between 1 and 5, hypophosphite ions in concentrations between 2 and 7 grams/liter, the substance which provides said hypophosphite ions being the only reducing agent for said salts in said solution, sufficient hydroxyl ions to maintain the pH at least 8, and one or more complexing or sequestering agents for forming stable water soluble complexes with the nickel and iron ions of said salts. 70
 2. A solution as claimed in claim 1, in which one of said agents contains sufficient ammonium ions to form the nickel hexamine complex ion with the nickel ions. 75
 3. A solution as claimed in claim 2, in which the concentration of the ammonium ions is between 0.6 and 300 grams/liter. 80
 4. A solution as claimed in any preceding claim, in which one of said agents contains tartrate ions. 85
 5. A solution as claimed in claim 4, in which the concentration of the tartrate ions is between 5 and 80 grams/liter. 90
 6. A solution as claimed in claim 1, in which one of said agents is organic and has an amino, imino, carboxy or hydroxy radical. 95
 7. A solution as claimed in any one of the preceding claims, in which the concentration of the nickel ions is between 0.3 and 30 grams/liter. 100
 8. A solution as claimed in any one of the preceding claims, in which the concentration of the ferrous ions is between 0.1 and 10 grams/liter. 105
 9. An aqueous solution for electrolessly depositing magnetic material containing nickel and iron, substantially as herein described with reference to CHARTS 1 and 2 and the examples. 110
 10. An electroless plating process in which an aqueous solution as claimed in any of the preceding claims is used for carrying out the process. 115
 11. An article plated by a process as claimed in claim 10. 120
 12. An article as claimed in claim 11, the process resulting in the plating of the article with an alloy comprising 15 to 35 percent by 125
 - 130

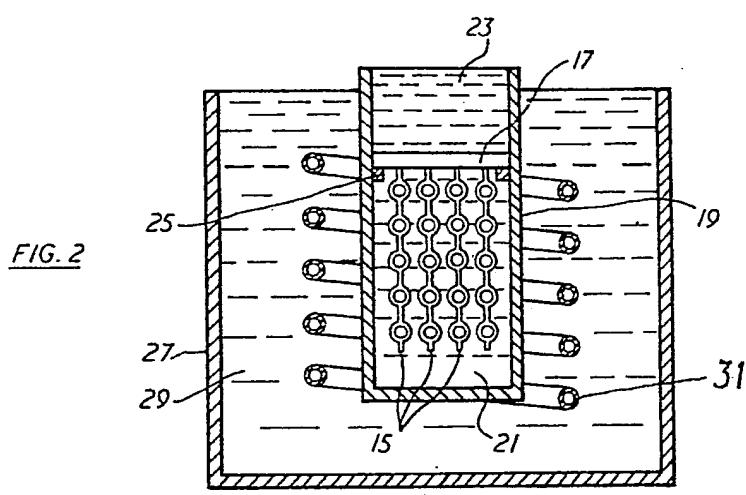
weight of iron, 0.25 to 2 percent by weight of phosphorous, and the balance nickel.

J. D. LANCASTER,
Chartered Patent Agent,
Agent for the Applicants.

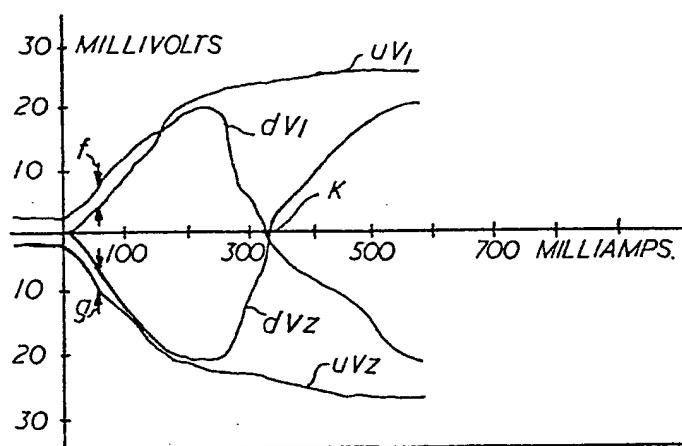
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O_2
 O_1
 B_r
(MAXWE)



6
4
2
 H_c
(oe)



300
200
100
(ma)
CROSS
POINT

FIG. 3

1,052,646

2 SHEETS

COMPLETE SPECIFICATION

This drawing is a reproduction of
the Original on a reduced scale.
SHEETS 1 & 2

FIG. 4

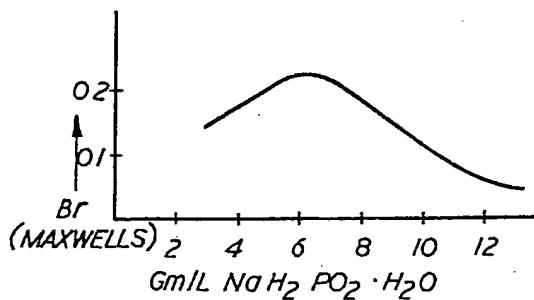


FIG. 7

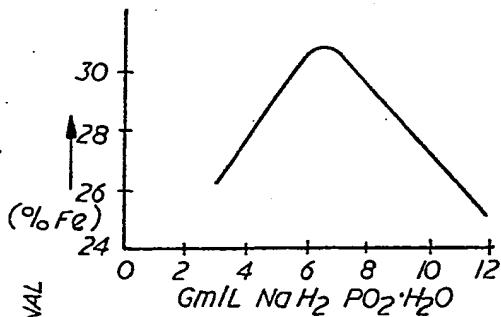


FIG. 5

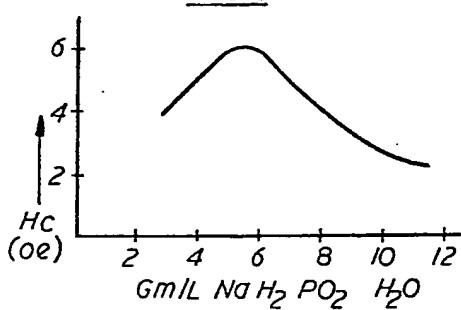


FIG. 8

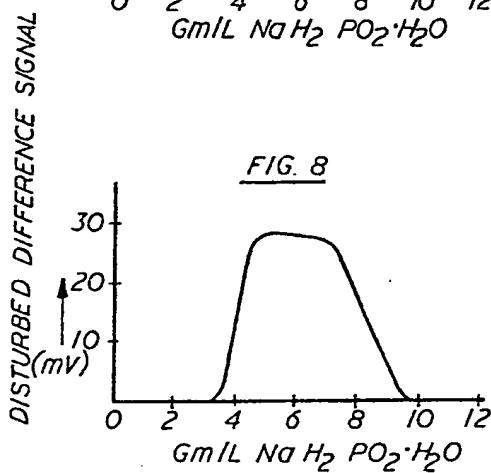


FIG. 6

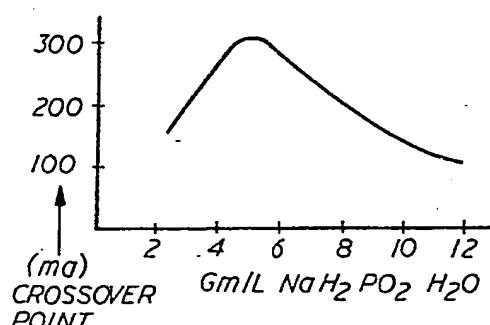
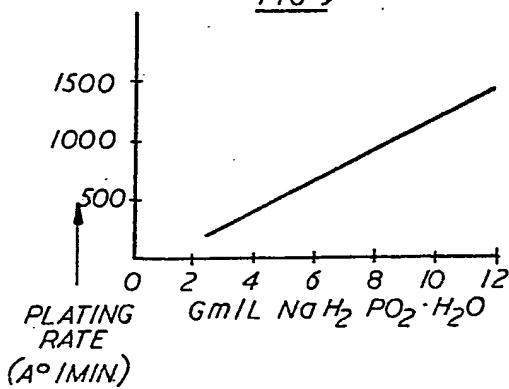


FIG. 9



1,052,646 COMPLETE SPECIFICATION
 2 SHEETS This drawing is a reproduction of
 the Original on a reduced scale.
 SHEETS 1 & 2

FIG 4

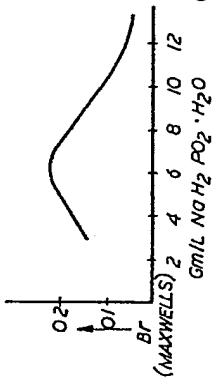


FIG 7

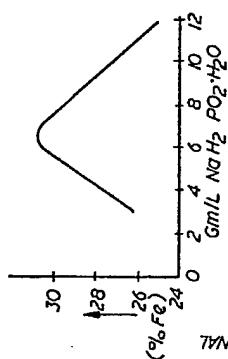


FIG 5

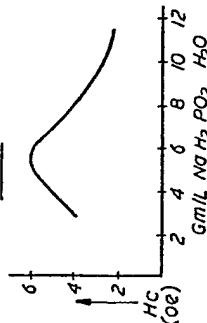


FIG 8

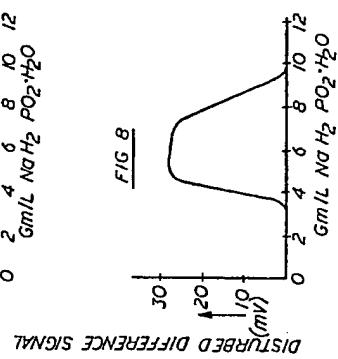


FIG 6

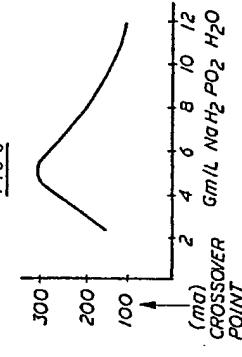


FIG 3

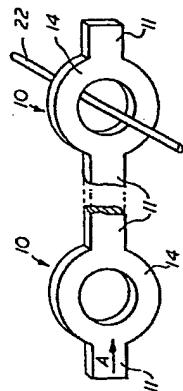
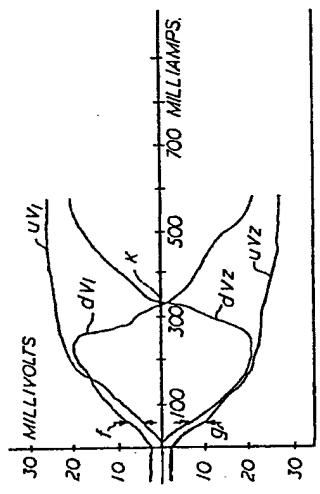


FIG 2

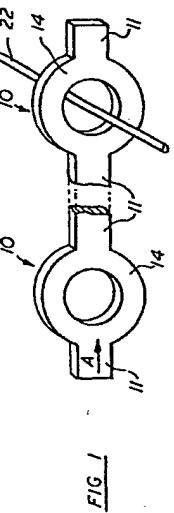


FIG 1

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : **NEC CORP**

(22)Date of filing : **22.02.1988**

(72)Inventor : **MARUYAMA TAKAO**

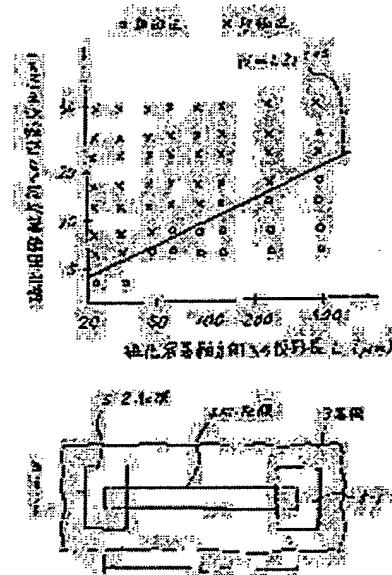
(54) MAGNETORESISTANCE ELEMENT

(57)Abstract:

PURPOSE: To obtain an element in which Barkhausen noise which has seriously harmful influence upon the operation of a magnetic head and a magnetic sensor does not appear by a method wherein the projected length L to the easy-to-magnetize axis direction and the projected length W to the difficult-to-magnetize axis direction of a magnetoresistance effect film whose basic pattern is a parallelogram conform to a specific inequality.

CONSTITUTION: The projected length L to the easy-to-magnetize axis direction and the projected length W to the difficult-to-magnetize axis direction of a magnetoresistance effect film whose basic pattern is a parallelogram conform to an inequality $0 < W < 1.2 \times L \times 0.45$. For instance, an Ni-Fe film 4 with a thickness of $0.04 \mu\text{m}$ is formed by vacuum evaporation on a substrate 3 obtained by oxidizing the surface of an Si chip to form a rectangular magnetoresistance effect film and Au films 5-1 and 5-2 are provided on both the ends of the rectangular film as electrodes. The magnetoresistance effect films with various long side lengths L and short side lengths

W are experimentally produced and relations to the number of magnetic domains which are shown in the diagram are obtained. Therefore, if the shape of the magnetoresistance effect film conforms to the inequality $0 < W < 1.2 \times L \times 0.45$, a magnetic wall does not exist so that the Barkhausen noise of the magnetoresistance effect film can be eliminated.



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